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Supplement of

On-line solid phase microextraction derivatization for the sensitive determination of multi-oxygenated volatile compounds in air

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Figure SI.1 Derivatization reactions of multi-oxygenated compounds.

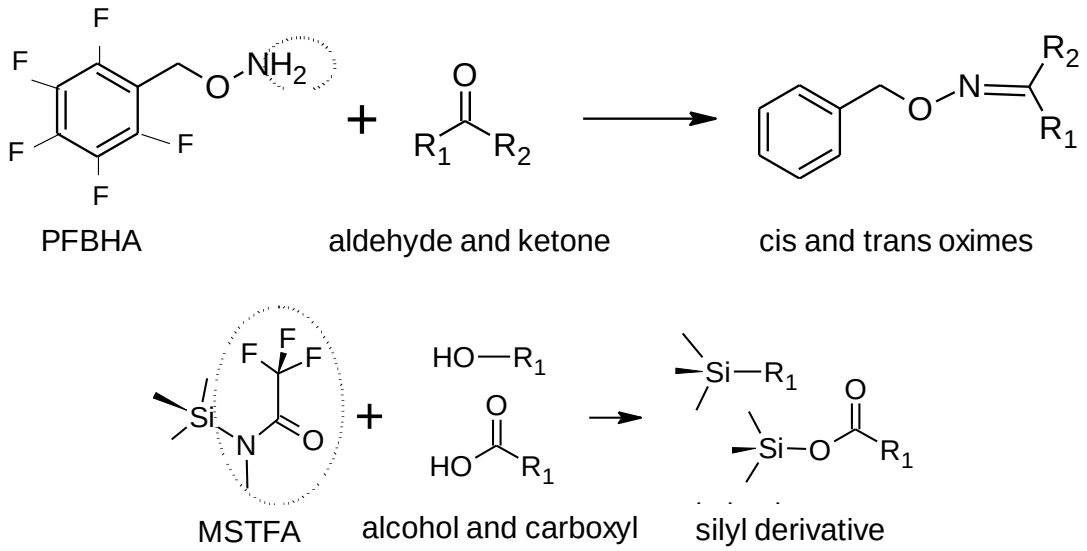
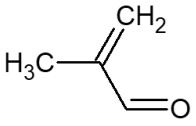


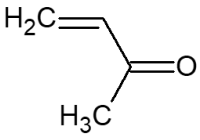
Table SI.1. A detailed description of techniques and institutions that participated in the OVOCs intercomparison of EUROCHAMP project.

Instrumentation Analysis Technique	**Institute Name**	**ID**
On-line SPME-GCMS plus derivatization	CEAM Foundation	CEAM
FTIR		
DNPH cartridges analyzed by LC-MS		
PTR-ToF-MS	Forschungszentrum Jülich	FZJ
SIFT-MS	University of York	York
PTR-ToF-MS	Leeds University	Leeds

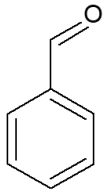
Figure SI.2 The structures of carbonyl model compounds



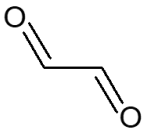
Methacrolein
MW:70



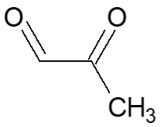
Methyl vinyl ketone
MW:70



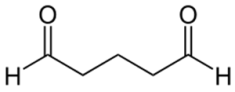
Benzaldehyde
MW:106



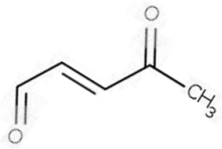
Glyoxal
MW:58



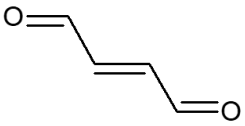
Methyl glyoxal
MW:72



Glutaraldehyde
MW:100



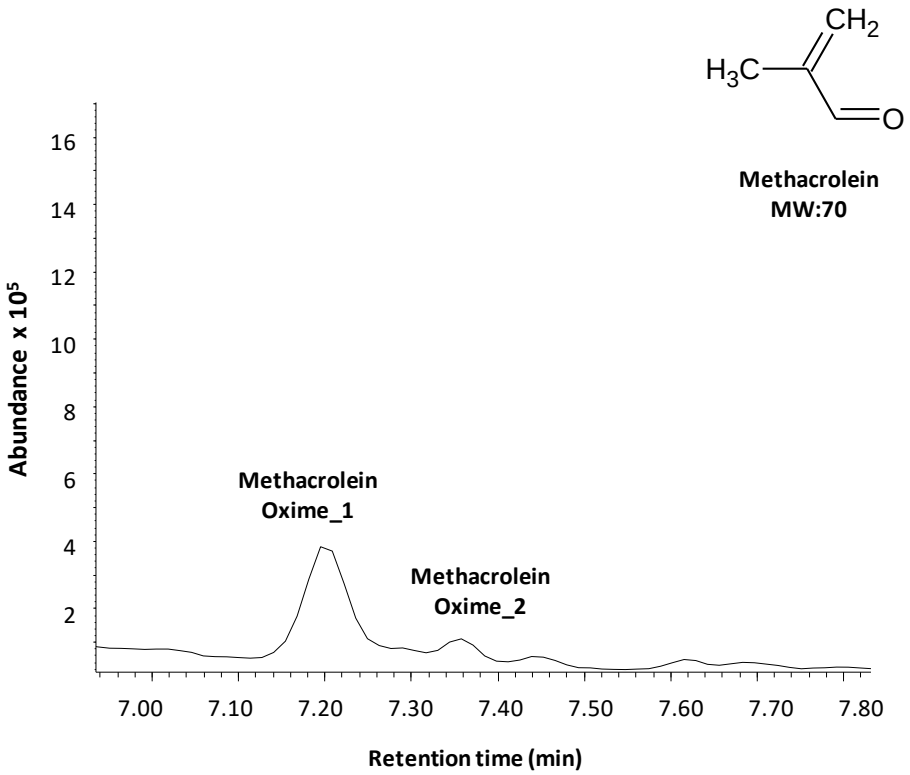
4-Oxo-2-pentenal
MW:98



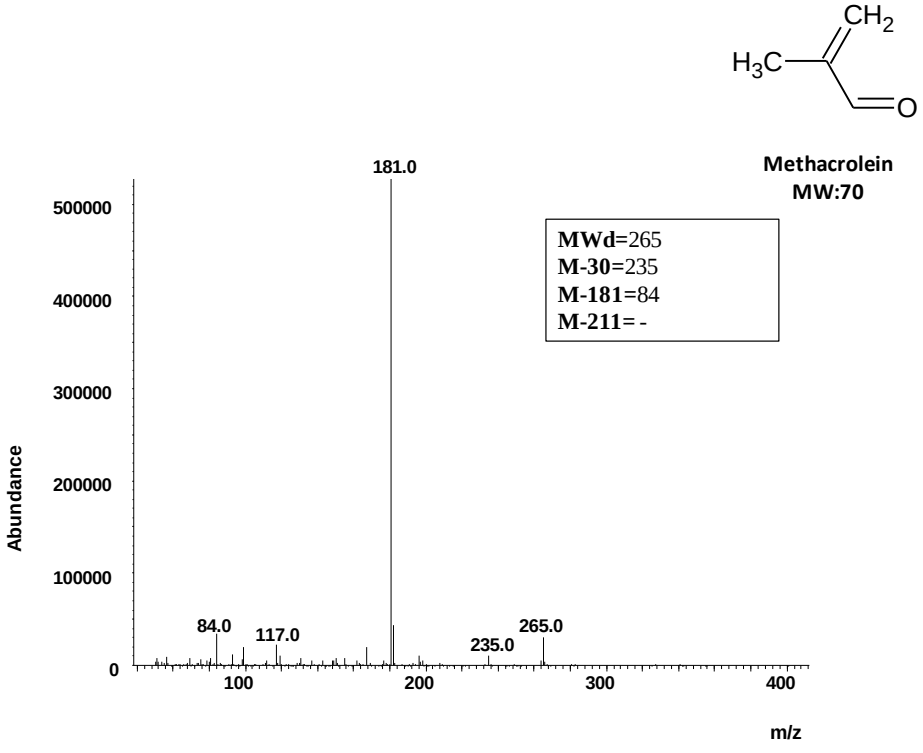
Butenedial
MW:86

Figure SI. 3 The chromatograms of oxime peaks of each carbonyl compound and its corresponding mass spectra.

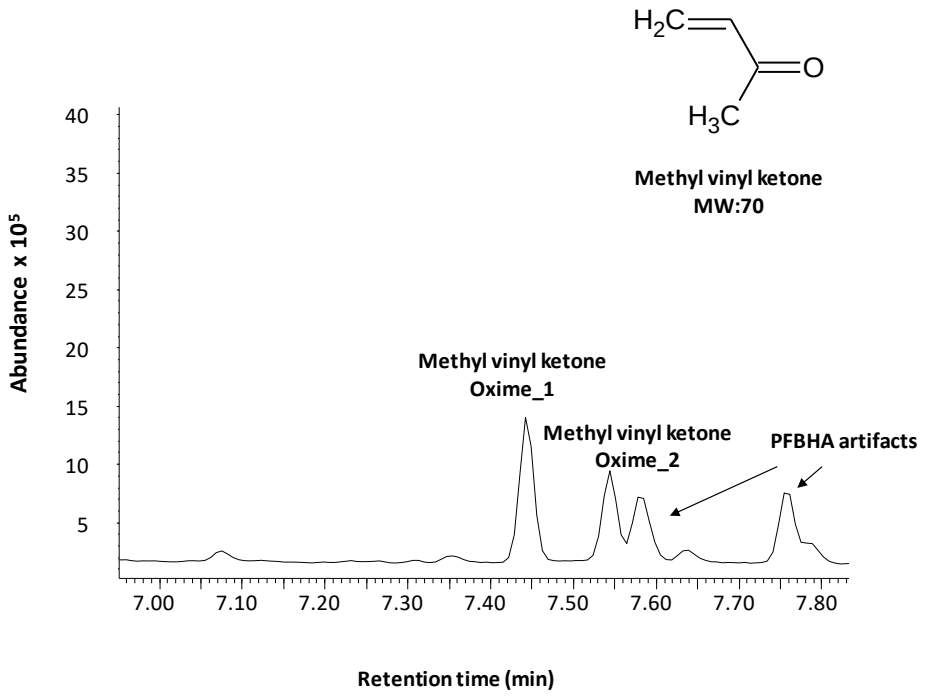
a)



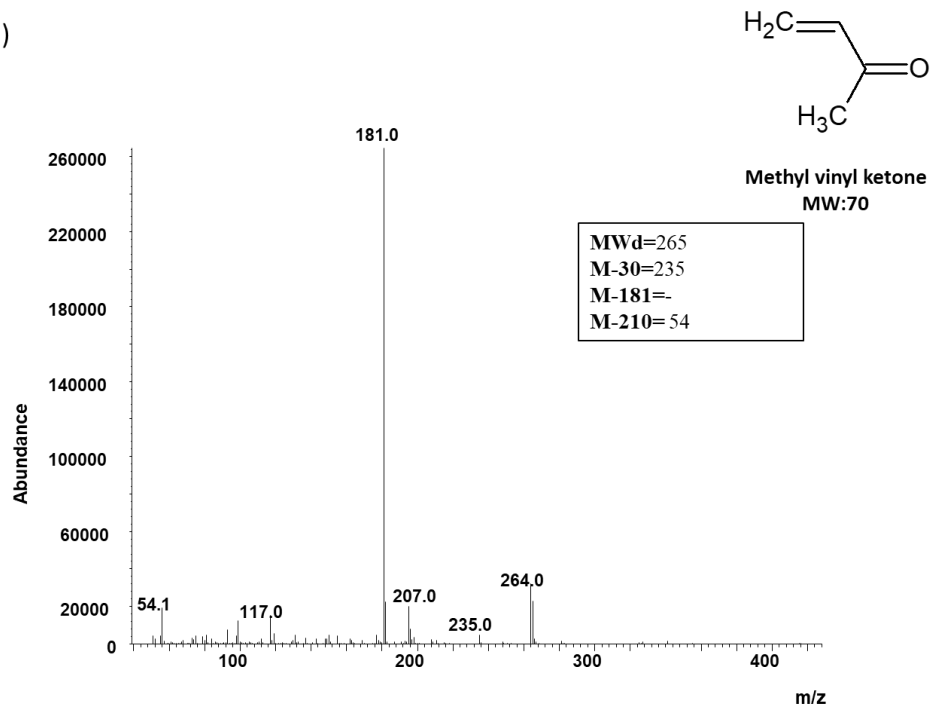
b)



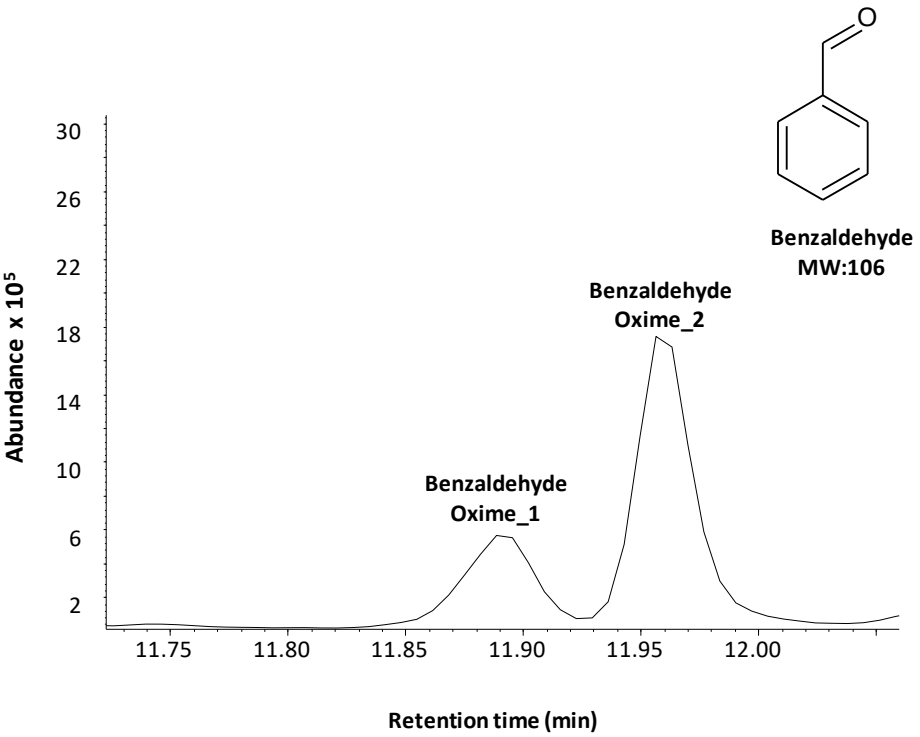
c)


H2C
O
H3C
Methyl vinyl ketone
MW:70
Abundance x 10^5
40
35
30
25
20
15
10
5
Methyl vinyl ketone
Oxime_1
Methyl vinyl ketone
Oxime_2
PFBHA artifacts
7.00
7.10
7.20
7.30
7.40
7.50
7.60
7.70
7.80
Retention time (min)

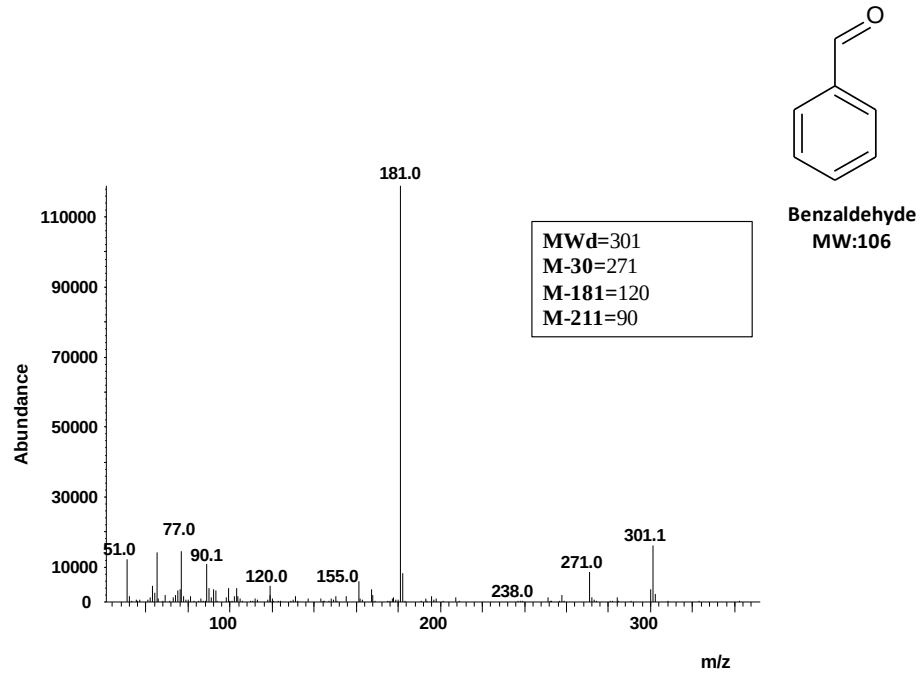
d)


H2C
O
H3C
Methyl vinyl ketone
MW:70
MWd=265
M-30=235
M-181=-
M-210= 54
Abundance
260000
220000
180000
140000
100000
60000
20000
0
181.0
264.0
207.0
54.1
117.0
235.0
100
200
300
400
m/z

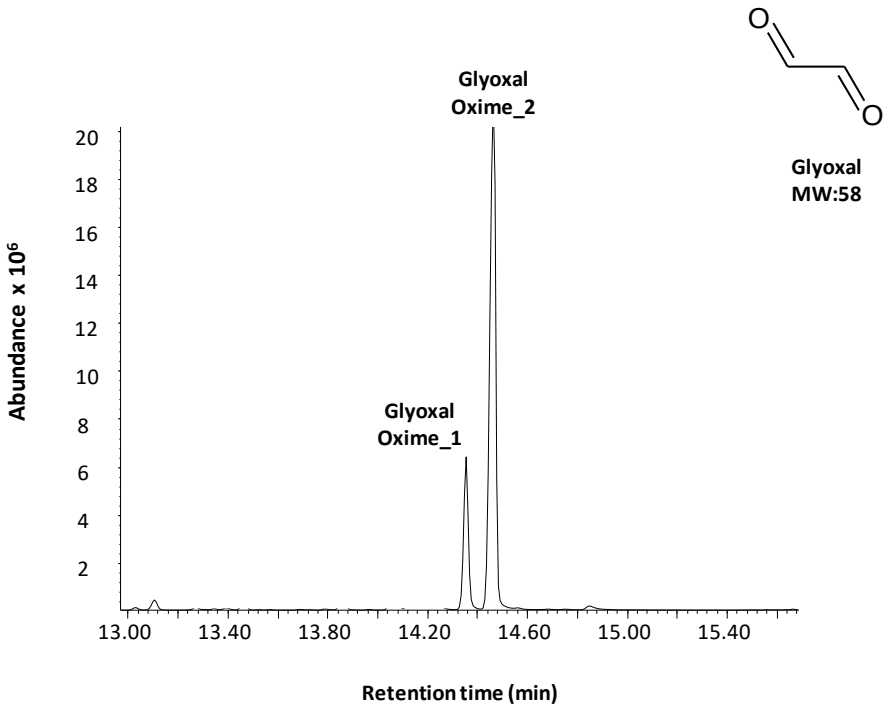
e)


O
Benzaldehyde
MW:106
Benzaldehyde
Oxime_2
Benzaldehyde
Oxime_1
Abundance x 10^5
30
26
22
18
14
10
6
2
11.75
11.80
11.85
11.90
11.95
12.00
Retention time (min)

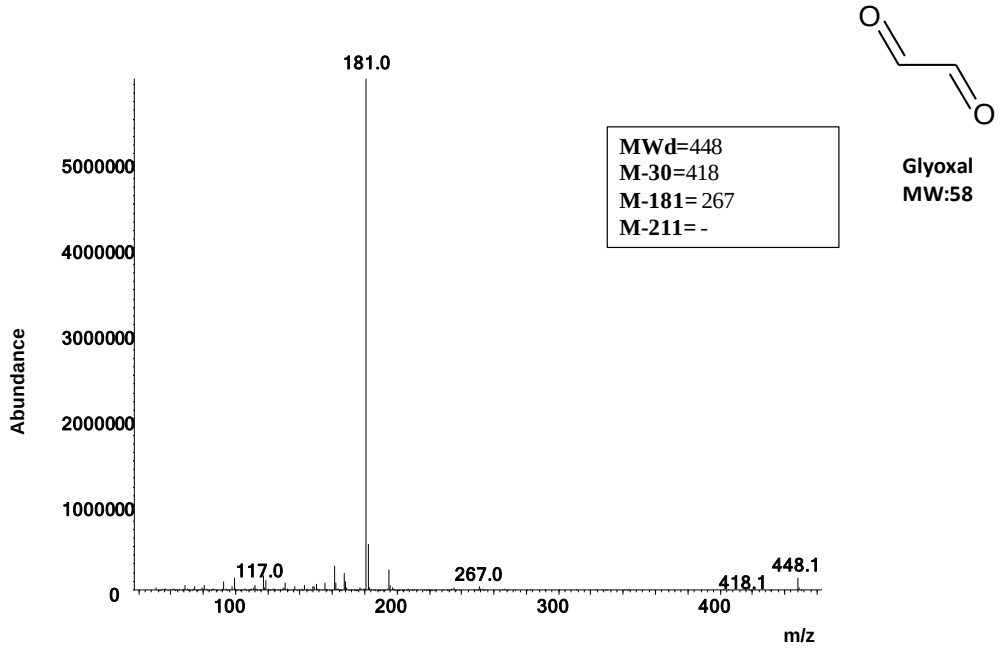
f)


O
Benzaldehyde
MW:106
181.0
MWd=301
M-30=271
M-181=120
M-211=90
Abundance
110000
90000
70000
50000
30000
10000
0
51.0
77.0
90.1
120.0
155.0
238.0
271.0
301.1
100
200
300
m/z

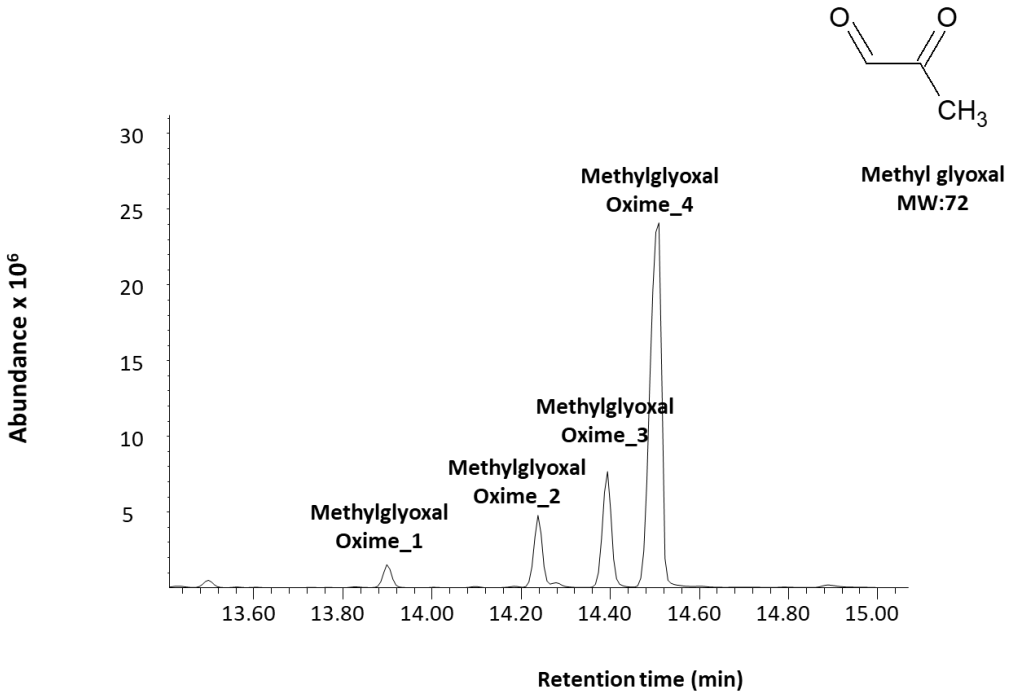
g)


Glyoxal
Oxime_2
Glyoxal
Oxime_1
Abundance x 10^6
20
18
16
14
12
10
8
6
4
2
13.00
13.40
13.80
14.20
14.60
15.00
15.40
Retention time (min)
O
O
Glyoxal
MW:58

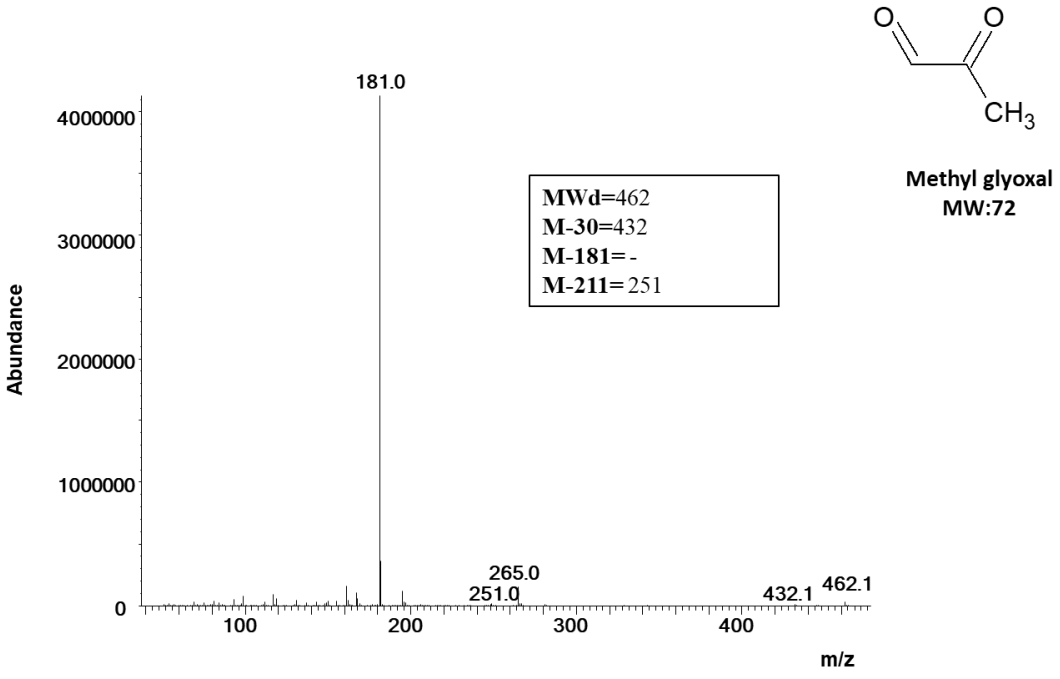
h)


181.0
MWd=448
M-30=418
M-181= 267
M-211= -
Abundance
5000000
4000000
3000000
2000000
1000000
0
117.0
267.0
418.1
448.1
100
200
300
400
m/z
O
O
Glyoxal
MW:58

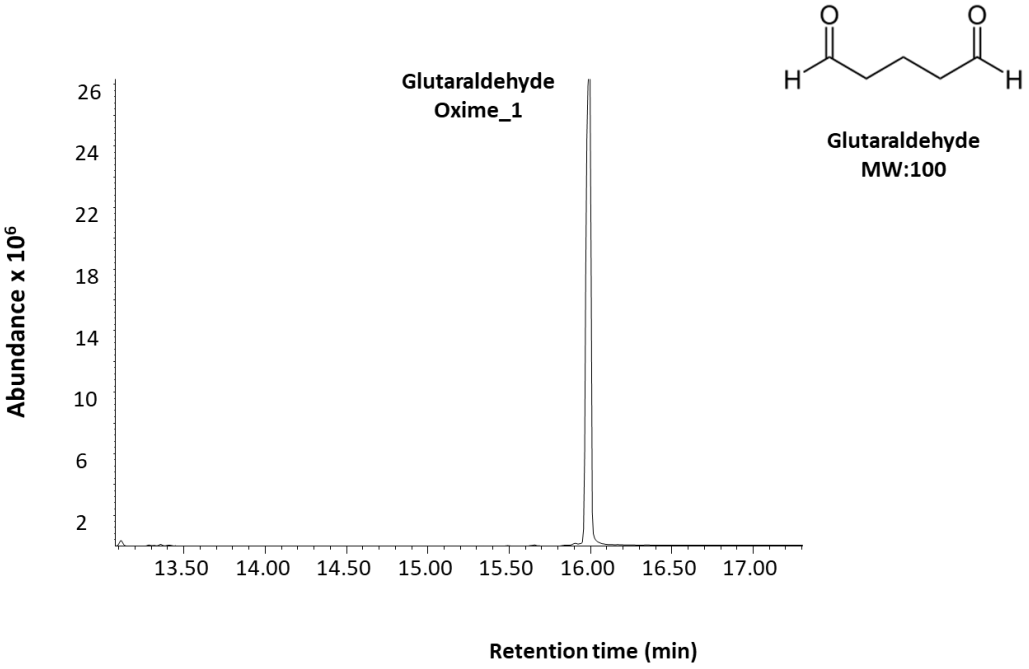
i)


O
O
CH3
Methyl glyoxal
MW:72
Methylglyoxal
Oxime_4
Methylglyoxal
Oxime_3
Methylglyoxal
Oxime_2
Methylglyoxal
Oxime_1
Abundance x 10^6
30
25
20
15
10
5
13.60
13.80
14.00
14.20
14.40
14.60
14.80
15.00
Retention time (min)

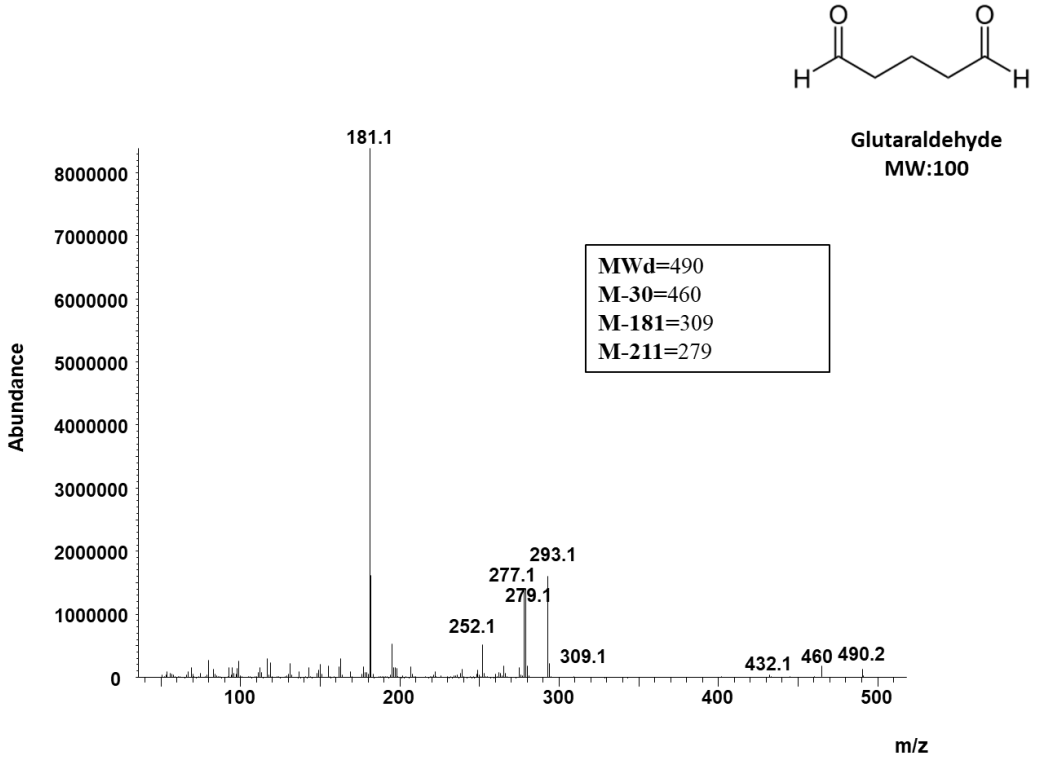
j)


O
O
CH3
Methyl glyoxal
MW:72
181.0
MWd=462
M-30=432
M-181=-
M-211=251
Abundance
4000000
3000000
2000000
1000000
0
265.0
251.0
432.1
462.1
100
200
300
400
m/z

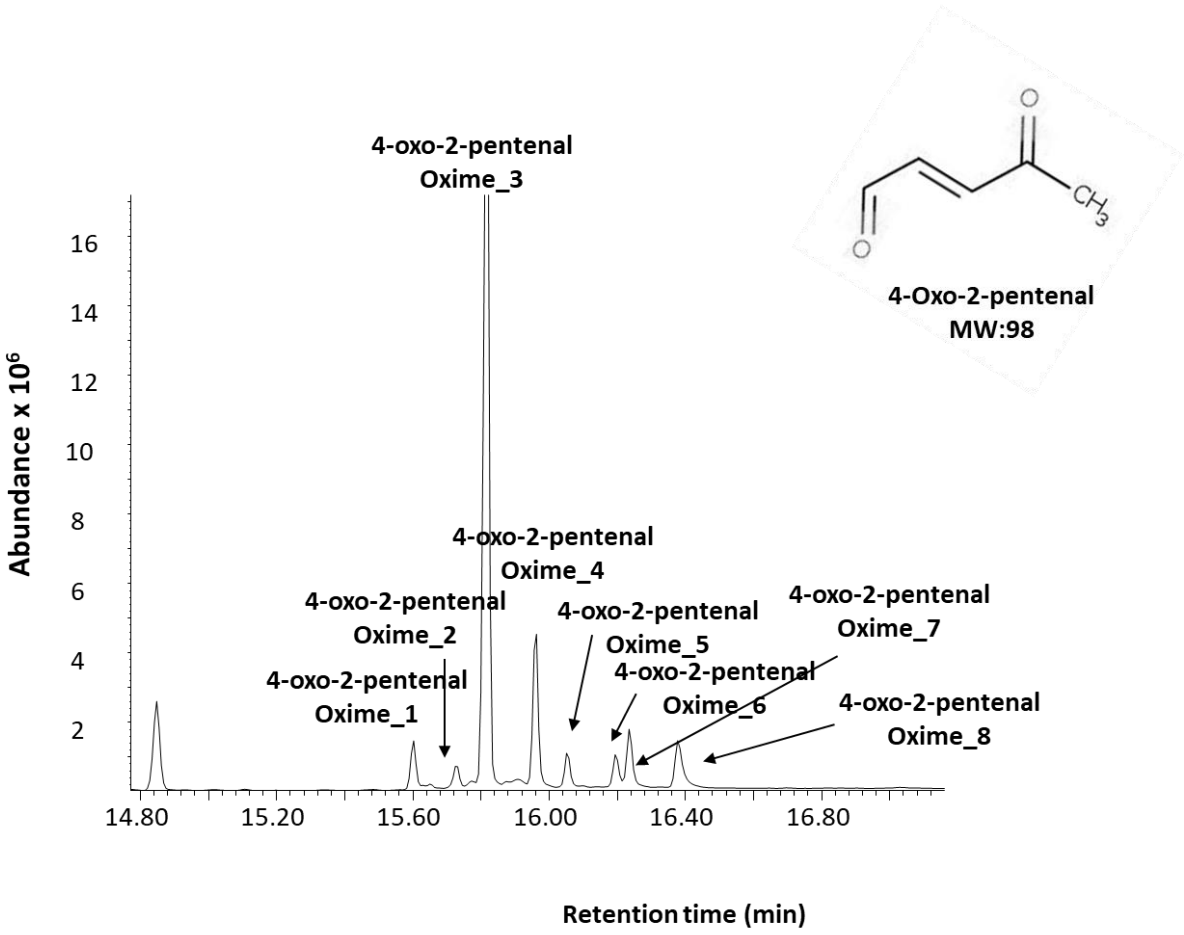
k)


Glutaraldehyde
Oxime_1
Abundance x 10^6
26
24
22
18
14
10
6
2
13.50
14.00
14.50
15.00
15.50
16.00
16.50
17.00
Retention time (min)
O
O
H
H
Glutaraldehyde
MW:100

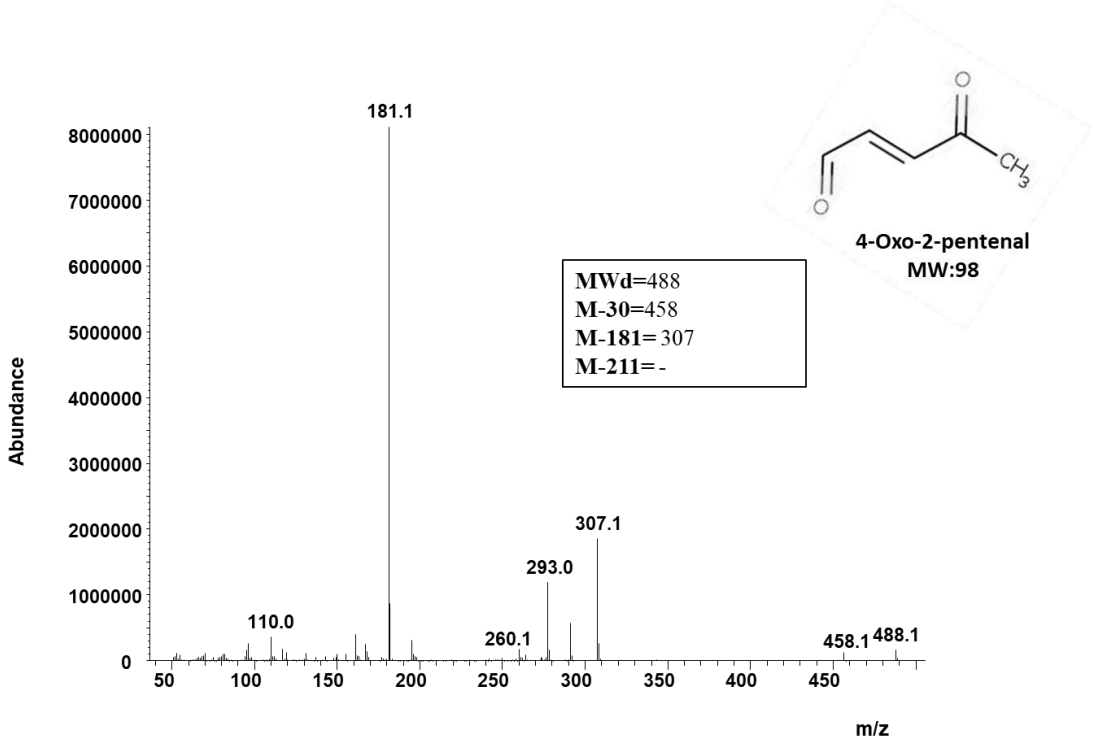
l)


181.1
Abundance
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
293.1
277.1
279.1
252.1
309.1
432.1
460
490.2
100
200
300
400
500
m/z
MWd=490
M-30=460
M-181=309
M-211=279
O
O
H
H
Glutaraldehyde
MW:100

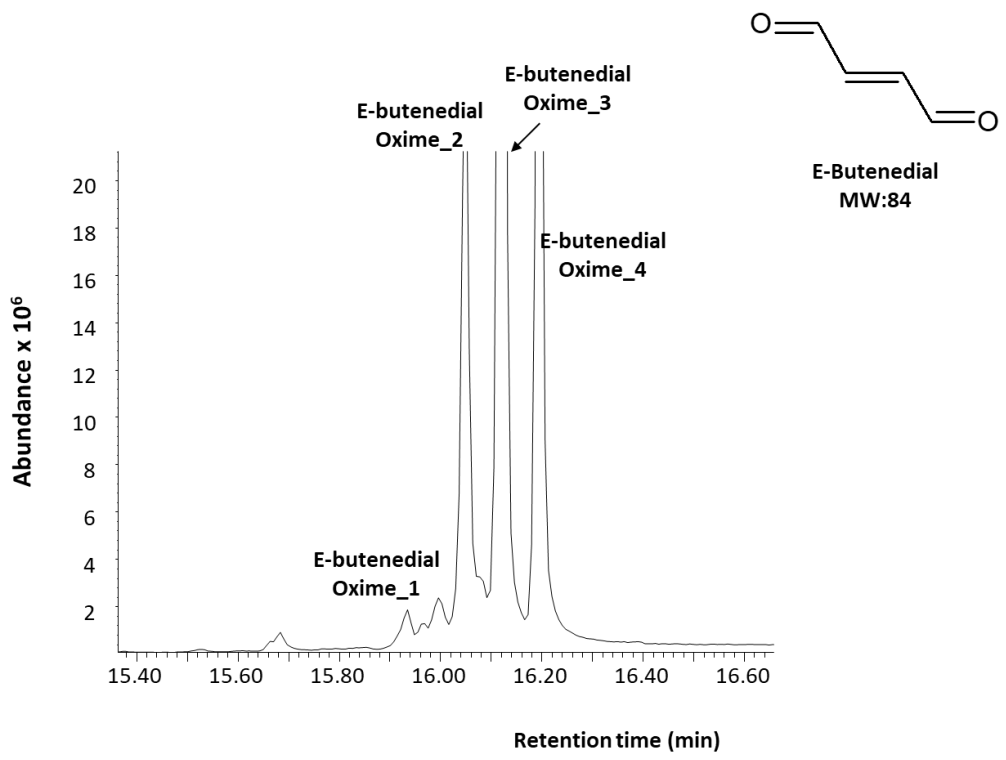
m)


4-oxo-2-pentenal
Oxime_3
4-oxo-2-pentenal
Oxime_4
4-oxo-2-pentenal
Oxime_2
4-oxo-2-pentenal
Oxime_5
4-oxo-2-pentenal
Oxime_7
4-oxo-2-pentenal
Oxime_1
4-oxo-2-pentenal
Oxime_6
4-oxo-2-pentenal
Oxime_8
Abundance x 10^6
16
14
12
10
8
6
4
2
14.80
15.20
15.60
16.00
16.40
16.80
Retention time (min)
4-Oxo-2-pentenal
MW:98

n)


181.1
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
Abundance
MWd=488
M-30=458
M-181= 307
M-211= -
307.1
293.0
110.0
260.1
458.1
488.1
50
100
150
200
250
300
350
400
450
m/z
4-Oxo-2-pentenal
MW:98

o)


E-butenedial
Oxime_3
E-butenedial
Oxime_2
E-butenedial
Oxime_4
E-butenedial
Oxime_1
Abundance x 10^6
20
18
16
14
12
10
8
6
4
2
15.40
15.60
15.80
16.00
16.20
16.40
16.60
Retention time (min)
O
O
E-Butenedial
MW:84

p)

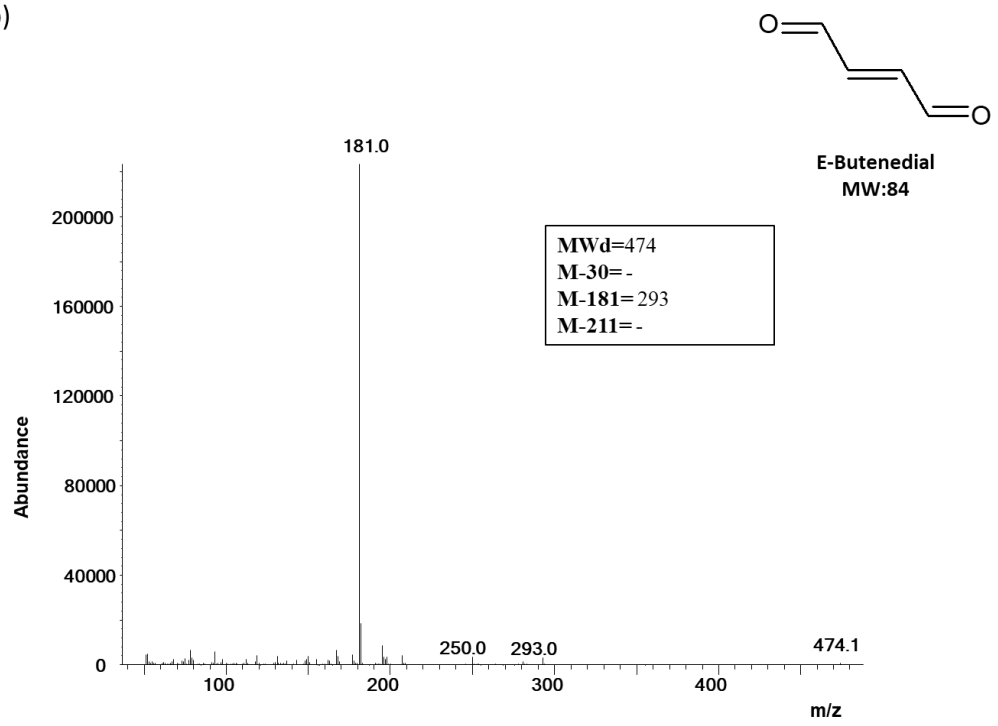

181.0
200000
160000
120000
80000
40000
0
Abundance
MWd=474
M-30= -
M-181= 293
M-211= -
250.0
293.0
474.1
100
200
300
400
m/z
O
O
E-Butenedial
MW:84

Table SI.2 The calculated recoveries of 8 OVOCs mixture.

Compound	*R.F*	R^2	$[\ ]_{theoretical}$ *(ppbV)*	$[\ ]_{experimental}$ *(ppbV)*	*Losses partial derivatization (%)*	*Recovery main oxime (%)*
Methacrolein	9027	0.982	45	44	0.0	99.0
Methyl vinyl ketone	8046	0.971	59	57	0.0	97.1
Benzaldehyde	19776	0.985	71	69	0.0	96.6
Glyoxal	427247	0.992	40	40	0.3	99.5
Methylglyoxal	4390256	0.997	45	45	0.2	99.7
E-4-oxo-2-pentenal	6273254	0.990	15	14	0.5	95.9
Glutaraldehyde	10465617	0.952	27	25	1.6	91.3
E-butenedial	4863653	0.982	10	10	0.6	99.0

R.F: response factor

Table SI. 3 Optimization experiments of on-fiber MSTFA derivatization after on-fiber PFBHA derivatization. Peaks: glycolaldehyde isomer 1 (8.2 min, MWd 327), glycolaldehyde isomer 2 (8.3 min, MWd 327), hydroxyacetone isomer 1 (9.8 min, MWd 341), hydroxyacetone isomer 2 (9.9 min, MWd 341), succinic acid (10.4 min, MWd: 262).

Step	*Variable*	*Range*	*Selected value*
Headspace generation	MSTFA concentration	10 – 100 µL	40 µL
	TMCS Catalyst	1 – 20 µL	5 µL
	Loading temperature	20 – 50 ºC	50 ºC
	Agitation time	1– 10 min	3 min
	Agitation speed	200 – 500 rpm	500 rpm
Reagent loading	Loading time	1– 10 min	3 min
Desorption	Time	1-15 min	10 min
	Temperature	150 – 250ºC	250ºC